Chapter 7
Mercury in Plankton

7.1 Results

Phytoplankton and zooplankton were collected in Lake Michigan from June 1994 through October 1995 for total mercury analysis. Phytoplankton samples were collected by pumping water from the optimum depth in the water column for maximum phytoplankton density through 10-µm phytovibe nets. Zooplankton samples were collected in vertical tows using nested 102-µm and 500-µm plankton nets (see Section 2.4.5 for details of the sample collection procedures). Plankton samples were collected from 15 locations, including 9 stations within 4 designated biological sampling areas (biota boxes) and 6 additional routine monitoring stations (see Figure 2-7 in Chapter 2). A total of 157 samples were collected and analyzed for total mercury by cold vapor atomic fluorescence spectroscopy (Table 7-1).

7.1.1 Variation Among Sample Types

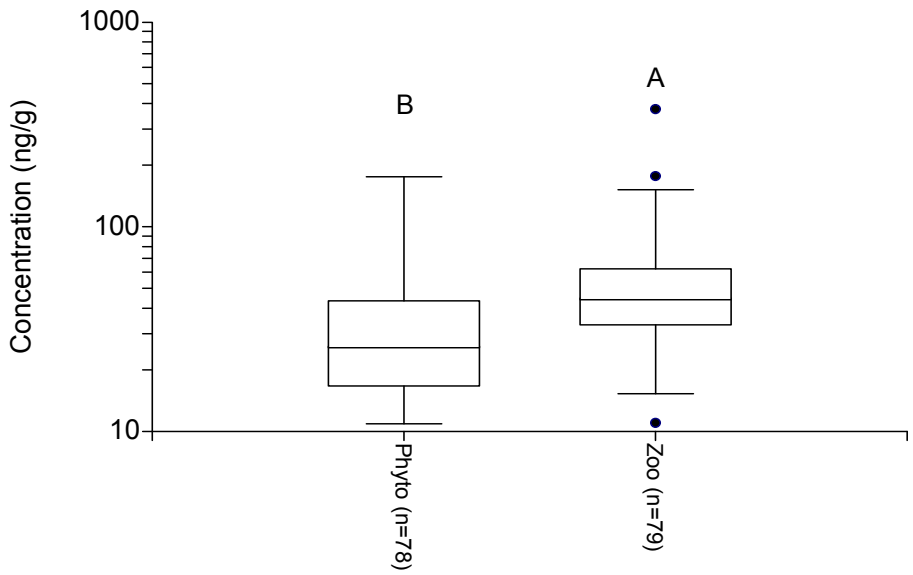
All plankton samples collected from Lake Michigan, except one zooplankton sample, contained total mercury levels above sample-specific detection limits, which averaged 8.65 ng/g for phytoplankton and 7.82 ng/g for zooplankton. Total mercury concentrations in phytoplankton ranged from 10.9 to 176 ng/g and averaged 35.0 ng/g. Total mercury concentrations in zooplankton ranged from 11.0 to 376 ng/g and averaged 54.3 ng/g. Based on a paired *t*-test using log-transformed mercury data, Lake Michigan zooplankton contained significantly higher (at the 95% confidence level) levels of mercury than phytoplankton (Figure 7-1).

The significantly higher levels of mercury found in zooplankton compared to phytoplankton suggest the bioaccumulation and biomagnification of mercury in the lower pelagic food web of Lake Michigan. PCBs and *trans*-nonachlor also were found to bioaccumulate and biomagnify in the Lake Michigan food web (USEPA, 2004). For PCBs and *trans*-nonachlor, a portion of the difference between zooplankton and phytoplankton concentrations was due to the lipid content in the two groups. This was not true for mercury accumulation. Mercury concentrations in zooplankton and phytoplankton were not correlated with lipid content (r^2 of 5% and 0.9% for phytoplankton and zooplankton, respectively), and generalized linear model results showed that lipid content did not explain a significant portion of variability in mercury data either directly, or through interaction with trophic level (phytoplankton/zooplankton). While organic contaminants such as PCBs and *trans*-nonachlor are preferentially accumulated in fatty tissues, mercury does not appear to be preferentially accumulated in such tissues. Mercury has been shown to preferentially bind to sulfhydryl groups in proteins, and in fish, accumulate in muscle tissue (USEPA, 1999b).

Table 7-1. Number of Plankton Samples Analyzed for Mercury in the LMMB Study

Sample Type	Sampling Location		Sampling Dates	Number of Samples Analyzed
	Biota Box	Station		
Phytoplankton	Chicago biota box	05	06/26/94 to 10/10/95	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	6
		140	06/18/94 to 09/23/95	6
		180	06/18/94 to 09/22/95	6
	Port Washington biota box	240	06/21/94 to 10/02/95	5
		280	06/20/94 to 10/01/95	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6
		340	06/25/94 to 10/06/95	6
		380	06/24/94 to 10/06/95	7
	Other	18M	06/22/94 to 10/08/95	6
		23M	06/23/94 to 10/03/95	6
		27M	06/20/94 to 08/10/95	3
		40M	08/12/94 to 04/12/95	3
		47M	06/17/94 to 09/19/95	5
	Total			78
Zooplankton	Chicago biota box	05	06/26/94 to 10/10/95	7
	Sturgeon Bay biota box	110	06/19/94 to 09/23/95	6
		140	06/18/94 to 09/23/95	6
		180	06/18/94 to 09/22/95	5
	Port Washington biota box	240	06/21/94 to 10/02/95	6
		280	06/20/94 to 10/01/95	6
	Saugatuck biota box	310	06/26/94 to 10/08/95	6
		340	06/25/94 to 10/06/95	6
		380	06/24/94 to 10/06/95	7
	Other	18M	06/22/94 to 10/08/95	6
		23M	08/19/94 to 10/03/95	5
		27M	06/20/94 to 08/10/95	4
		40M	10/18/94 to 04/12/95	2
		47M	06/17/94 to 09/19/95	6
		19M	01/24/95 to 01/24/95	1
	Total			79
Total				157

Figure 7-1. Mercury Concentrations in Phytoplankton and Zooplankton Measured in Lake Michigan



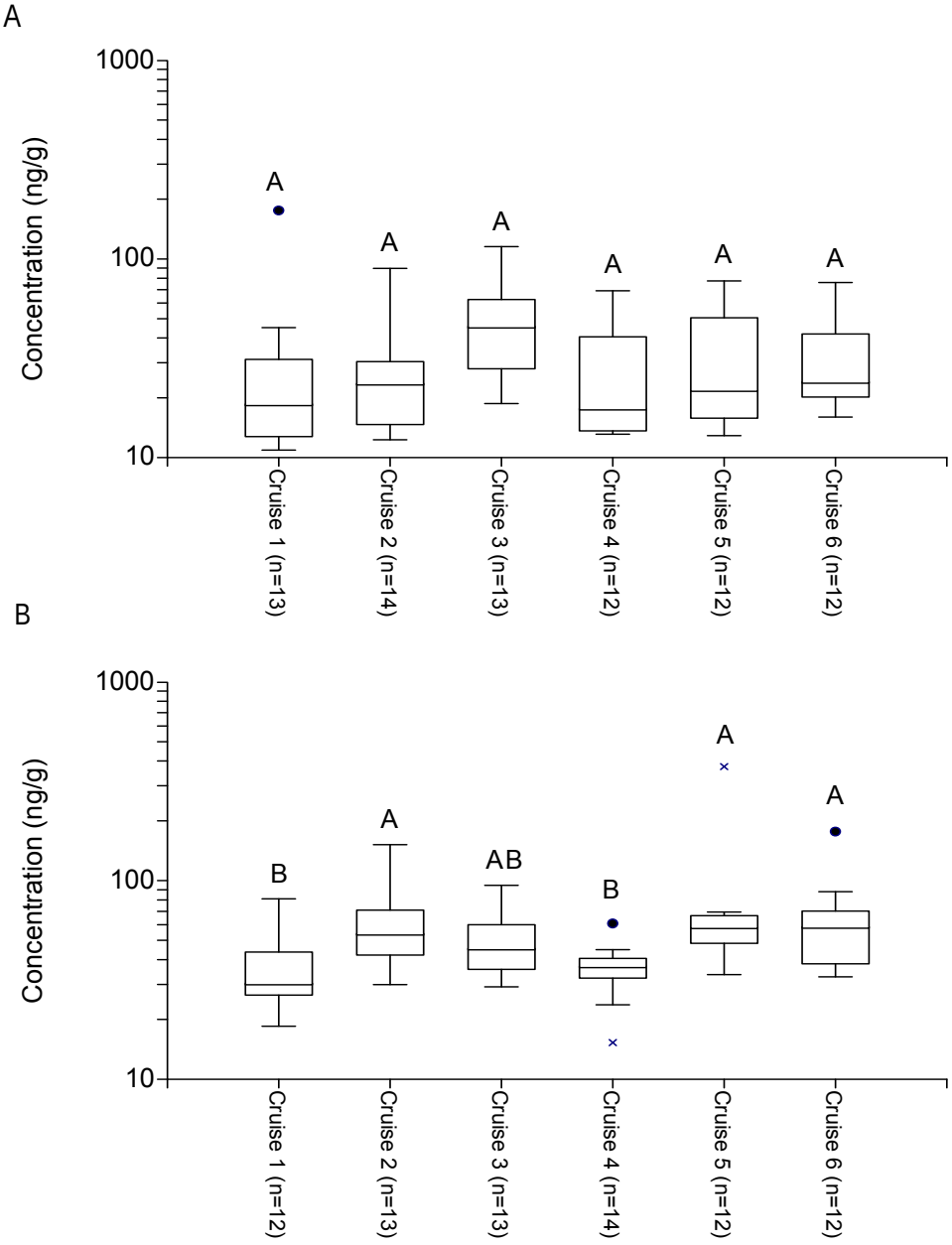
Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

7.1.2 Temporal Variation

Lake Michigan plankton were sampled in six separate cruises: June 1994, August 1994, September/October 1994, March/April 1995, August 1995, and September/October 1995. Two-way analysis of variance (accounting for cruise and sampling station) was conducted on log-transformed mercury data to evaluate temporal and geographical trends. This analysis revealed that total mercury concentrations in zooplankton differed significantly by cruise. In both sampling years, mercury concentrations in zooplankton were lowest in the spring (June 1994 and March/April 1995), peaked in late summer (August 1994 and August 1995), and remained elevated throughout the fall (September/October 1994 and September/October 1995) (Figure 7-2). In each year, mercury concentrations were significantly higher (at the 95% confidence level) in late summer than in the spring. Zooplankton mercury concentrations in the fall were also higher than spring amounts, but this difference was only significant for 1995 fall results (Cruise 6).

Phytoplankton mercury concentrations also differed significantly among cruises, based on the two-way analysis of variance, however, Tukey's multiple comparisons test did not identify any individual comparisons as significantly different. In both years, phytoplankton mercury concentrations increased throughout the summer and were highest in the fall. Individual differences between cruises, however, were not identified as statistically significant.

Figure 7-2. Mercury Concentrations in Phytoplankton (A) and Zooplankton (B) Measured in Lake Michigan during Six Cruises



(Cruise 1 = June 1994, Cruise 2 = August 1994, Cruise 3 = September/October 1994, Cruise 4 = March/April 1995, Cruise 5 = August 1995, and Cruise 6 = September/October 1995)

Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

7.1.3 Geographical Variation

Plankton samples were collected from 15 sampling stations in Lake Michigan (see Figure 2-7 in Chapter 2). Nine of these sampling stations were focused in the following four biological sampling areas or biota boxes:

- **Chicago biota box** — around Station 5 in the southern Lake Michigan basin near Chicago
- **Sturgeon Bay biota box** — a combination of three stations (110, 140, and 180) on the western side of the northern Lake Michigan basin near Sturgeon Bay, Wisconsin
- **Port Washington biota box** — a combination of two stations (240 and 280) in the central Lake Michigan basin near Port Washington, Wisconsin
- **Saugatuck biota box** — a series of three stations (310, 340, and 380) on the eastern side of the southern Lake Michigan basin near Saugatuck, Michigan.

In addition to focused sampling in these areas, samples also were collected from six LMMB monitoring sites throughout the lake (Table 7-1). Table 7-2 shows the concentrations of total mercury measured in plankton collected from the various sampling locations.

Considering all 15 individual sampling stations, two-way analysis of variance (accounting for cruise and sampling station) revealed no significant differences among sampling stations in phytoplankton or zooplankton mercury concentrations (Figure 7-3). When combining data within biota boxes, phytoplankton mercury concentrations still did not vary significantly among the biota box stations. The highest individual (176 ng/g) and mean (46.9 ng/g) phytoplankton mercury concentrations were observed at the Saugatuck biota box, but this site also contained the greatest variability, and differences between this site and other sites were not statistically significant (at the 95% confidence level).

Zooplankton mercury concentrations did vary significantly among biota boxes, however, no distinct trend was observed. A significant interaction occurred between the biota box and cruise variables, such that significant differences between stations were cruise-dependent. During Cruise 1, zooplankton mercury concentrations at the Saugatuck biota box were significantly higher than at the Sturgeon Bay biota box. During Cruise 3, zooplankton mercury concentrations at the Port Washington biota box were significantly higher than at the Saugatuck biota box. During Cruise 6, zooplankton mercury concentrations at the Chicago biota box were significantly higher than at the Saugatuck biota box.

7.1.4 Bioaccumulation

Mercury is known to accumulate in living organisms at levels far above concentrations in the water column. The degree of this accumulation is often quantified by a bioaccumulation factor, which is the ratio of the concentration of pollutant in an organism to the concentration of that pollutant in the water. When pollutants are increasingly accumulated with each trophic level of a food chain (or biomagnified), a biomagnification factor can be used to quantify the degree of accumulation from one trophic level to the next. A biomagnification factor is the ratio of the concentration of pollutant in organisms at a particular trophic level to the concentration of that pollutant in the next lowest trophic level.

In the LMMB Study, bioaccumulation factors for mercury were calculated as the mean concentration of mercury in phytoplankton or zooplankton divided by the lake-wide mean concentration of total mercury in Lake Michigan. Concentrations of total mercury in Lake Michigan plankton were generally 10^5 times higher than total mercury concentrations in Lake Michigan water, which averaged 0.328 ng/L (or 0.000328 ng/g, assuming the density of water is 1 g/mL). Bioaccumulation factors from water to phytoplankton were 1.07×10^5 and from water to zooplankton were 1.66×10^5.

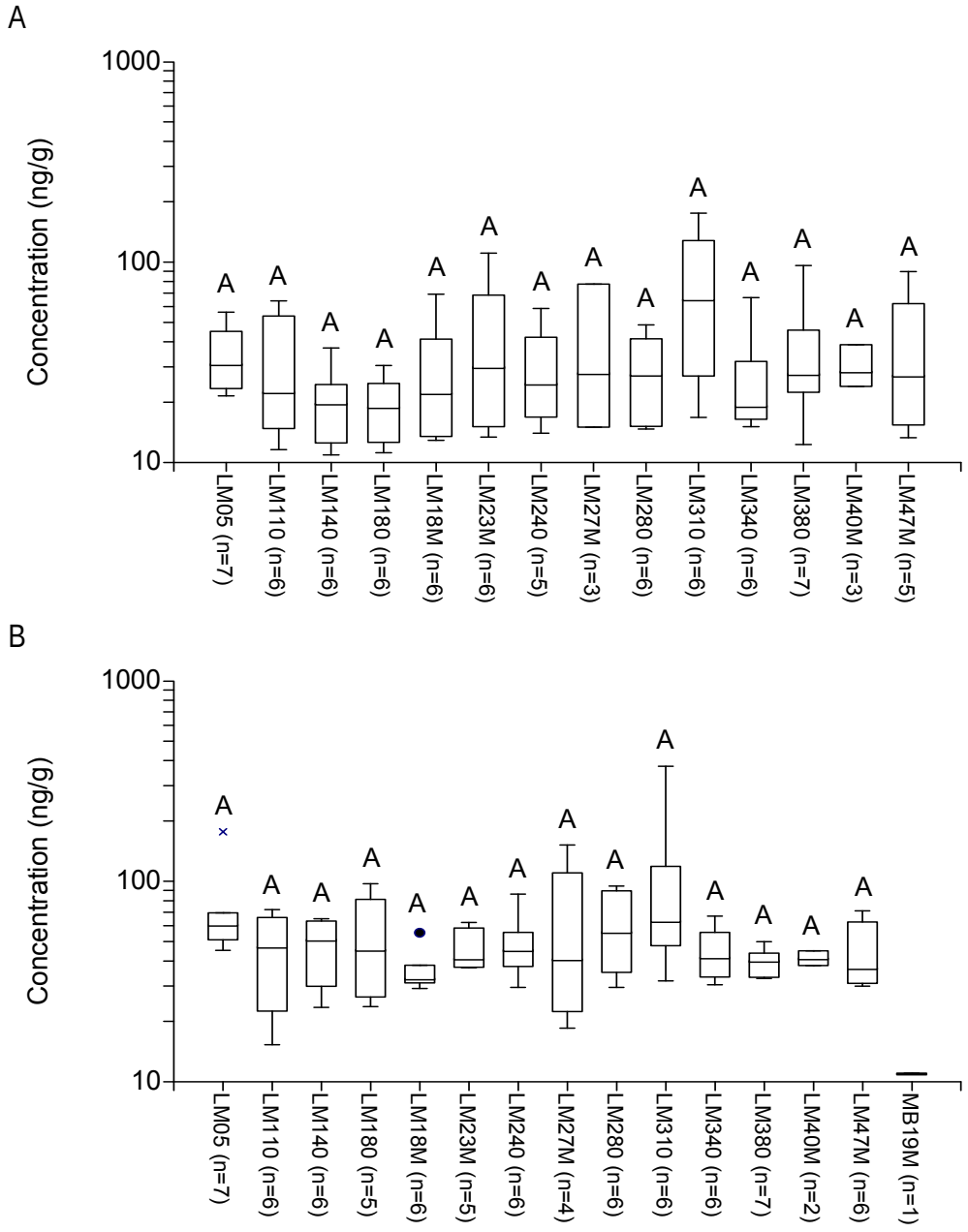
To evaluate the accumulation and transfer of mercury between trophic levels within the lower pelagic food web, biomagnification factors also were calculated. Biomagnification factors between primary producers and primary consumers were calculated as the concentration of contaminants in zooplankton divided by the concentration in phytoplankton. The biomagnification factor for mercury between phytoplankton and zooplankton was 1.55.

Table 7-2. Mercury Concentrations in Plankton Measured at Various Sampling Stations in Lake Michigan

Sample Type	Sampling Station		N	Mean (ng/g)	Range (ng/g)	SD (ng/g)	RSD (%)	Below DL (%)
	Biota Box	Station						
Phytoplankton	Chicago biota box	05	7	35.3	21.5 to 56.3	12.7	36.2	0
	Sturgeon Bay biota box	110	6	31.6	11.6 to 64.1	21.5	67.8	0
		140	6	20.4	10.9 to 37.3	9.31	45.7	0
		180	6	19.4	11.2 to 30.5	7.26	37.4	0
		combined	18	23.8	10.9 to 64.1	14.5	60.8	0
	Port Washington biota box	240	5	29.6	14.0 to 58.8	17.4	58.6	0
		280	6	28.8	14.7 to 48.7	13.3	46.3	0
		combined	11	29.2	14.0 to 58.8	14.5	49.6	0
	Saugatuck biota box	310	6	78.7	16.8 to 176	58.9	74.9	0
		340	6	27.0	15.1 to 66.6	19.7	72.9	0
		380	7	36.8	12.3 to 96.4	28.1	76.4	0
		combined	19	46.9	12.3 to 176	42.9	91.5	0
	Other	18M	6	29.4	12.9 to 69.2	21.3	72.6	0
		23M	6	44.2	13.4 to 111	37.7	85.2	0
		27M	3	40.2	15.0 to 77.7	33.1	82.2	0
		40M	3	30.4	24.0 to 38.7	7.53	24.8	0
		47M	5	38.2	13.3 to 89.9	31.0	81.2	0
Zooplankton	Chicago biota box	05	7	75.0	45.3 to 177	45.9	61.2	0
	Sturgeon Bay biota box	110	6	45.6	15.3 to 72.4	22.5	49.4	0
		140	6	47.8	23.5 to 65.1	16.7	34.9	0
		180	5	52.9	23.7 to 97.5	30.3	57.2	0
		combined	17	48.5	15.3 to 97.5	22.0	45.4	0
	Port Washington biota box	240	6	49.3	29.6 to 86.5	19.4	39.4	0
		280	6	60.5	29.6 to 94.8	26.9	44.5	0
		combined	12	54.9	29.6 to 94.8	23.1	42.1	0
	Saugatuck biota box	310	6	112	31.9 to 376	131	117	0
		340	6	44.7	30.5 to 67.2	13.5	30.1	0
		380	7	40.0	32.8 to 50.0	5.96	14.9	0
		combined	19	64.2	30.5 to 376	76.9	120	0
	Other	18M	6	36.0	29.2 to 55.4	9.65	26.9	0
		23M	5	46.7	37.1 to 62.4	11.4	24.5	0
		27M	4	63.1	18.5 to 152	60.2	95.4	0
		40M	2	41.5	38.0 to 45.0	4.95	11.9	0
		47M	6	44.5	30.0 to 71.3	17.2	38.6	0
		19M	1	11.0	NA	NA	NA	100

NA = Not applicable

Figure 7-3. Mercury Concentrations in Phytoplankton (A) and Zooplankton (B) Measured at Various Sampling Stations in Lake Michigan



Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

7.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of method quality objectives (MQOs) for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of plankton mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 7-3 provides a summary of flags applied to the plankton mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. No results were qualified as invalid, thus all results are represented in the analysis of plankton mercury concentrations presented in this report.

Table 7-3. Summary of Routine Field Sample Flags applied to Mercury in Plankton Samples

Flag	Number of QC Samples	Percentage of Samples Flagged
EHT, Exceeded Holding Time	—	75% (118)
FBS, Failed Blank Sample	18 lab reagent blank samples	44% (69)
FDL, Failed Lab Duplicate	31 lab duplicate samples	0
FFD, Failed Field Duplicate	38 field duplicate samples	4% (6)
FLS, Failed Lab Spike	11 lab fortified spiked samples	0
SCF, Suspected Field Contamination	—	1% (2)
UDL, Below Sample-Specific Detection Limit	—	1% (1)

The most frequently applied data validation flag was for exceeding sample holding times. Seventy-five percent of samples were analyzed beyond the 420-day established holding time. The median holding time for frozen plankton samples was 614 days, and frozen samples were held as long as 896 days prior to mercury analysis. The MQOs for holding times were based on educated, conservative assessments by the PIs, however, the appropriateness of these holding times has not been rigorously determined and the effects of extended holding times have not been investigated in the plankton matrix. Because phytoplankton samples were analyzed for total mercury, as opposed to the determination of mercury

species, possible conversion of mercury among individual species during the extended holding times would not likely affect total mercury measurements and loss of mercury would likely be negligible.

Laboratory reagent blanks were analyzed to assess the potential for contamination of routine field samples. A total of 18 laboratory reagent blanks were analyzed, and 11 of these 18 blanks contained detectable mercury. Forty-four percent of routine field samples were associated with (e.g., analyzed in the same batch) one of these 11 blanks that contained detectable mercury and were flagged for a failed blank (FBS). While 44% of routine field samples were flagged for associated blank failure, the maximum level of mercury detected in laboratory reagent blank samples was 0.1 ng/g, which is 100 times less than the lowest measured mercury concentration in plankton samples (10.9 ng/g). For this reason, contamination is not believed to significantly affect the reported plankton mercury results.

In addition to laboratory reagent blanks, laboratory dry blanks were analyzed at a frequency of 1 per 12 routine field samples. These blank results were not used to flag data, because they were not linked to specific routine field samples. Like laboratory reagent blanks, measured concentrations in laboratory dry blanks were 0.1 ng/g or below, further indicating that contamination did not significantly affect reported plankton mercury results. While blank sample analysis indicates no pervasive contamination, two samples were flagged for suspected field contamination based on a hydraulic fluid spill on the deck of the sampling vessel during the June 1994 sampling at Station 310.

A total of 38 field duplicate samples and 31 laboratory duplicate samples were analyzed to assess precision. From each cruise (except the January 1995 cruise that visited only two sites), duplicate samples were collected at one to six stations. Laboratory duplicates were prepared at a frequency of at least 2 per set of 24 routine field samples. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD or FDL) if the relative percent difference between results for a sample and its duplicate was greater than 30%. No laboratory duplicates failed to meet this criteria, and only 6 of the 38 field duplicates were flagged.

Laboratory fortified spike samples were used to monitor analytical bias, and no results were qualified for failed laboratory spikes. Based on an analysis of laboratory spikes, standard reference material recovery, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 7-4 provides a summary of data quality assessments for several of these attributes for plankton data. The results of laboratory and field duplicate samples revealed good system and analytical precision for plankton data. The mean RPD for field duplicate samples was 19.8% and the mean RPD for laboratory duplicate samples was 11.2%.

Analytical bias was evaluated by calculating the mean recovery of a standard reference material (SRM) from the National Institute of Standards and Technology and the mean recovery of laboratory fortified spike samples (LFS). Results indicated very little overall bias for analytical results. Mean recoveries for SRM 1515, an apple leaf sample with a certified value of 0.044 mg/kg, were 98%, and mean LFS recoveries were 103%, just slightly above and below the ideal recovery of 100%.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the sample-specific detection limit. Only one sample, or 0.6% of the data, was below the detection limit. Results

from this sample were not censored and were used as reported in the analysis of plankton mercury data presented in this report.

Table 7-4. Data Quality Assessment in Plankton Samples

Parameter	Number of QC Samples	Assessment
Number of Routine Samples Analyzed	—	157
System Precision, Mean Field Duplicate RPD (%), >MDL	38 field duplicate pairs	19.8%
Analytical Precision, Mean Lab Duplicate RPD (%), >MDL	28 lab duplicate pairs	11.2%
Analytical Bias, Mean SRM (%)	18 SRM samples	98%
Analytical Bias, Mean LFS (%)	11 LFS samples	103%
Analytical Sensitivity, Samples reported as <MDL (%)	—	0.6%

MDL = Sample-specific Detection Limit
SRM = Standard Reference Material
LFS = Laboratory Fortified Spike

7.3 Data Interpretation

7.3.1 Mercury Levels in Lake Michigan Plankton

In the LMMB Study, plankton mercury levels ranged from 10.9 to 376 ng/g and averaged 35.0 ng/g in phytoplankton and 54.3 ng/g in zooplankton. This is very similar to the average phytoplankton and zooplankton mercury concentrations of 30 and 56 ng/g, respectively, measured by Watras and Bloom (1992) in one basin of Little Rock Lake, in north-central Wisconsin. Little Rock Lake is divided into two separate basins, one of which has been experimentally acidified. Watras and Bloom (1992) measured slightly higher mercury concentrations (average of 40 ng/g for phytoplankton and 75 ng/g for zooplankton) in the acidified basin, compared to the reference basin.

Higher plankton mercury levels were also measured in numerous Wisconsin, Minnesota, and Canadian lakes. In Devil's Lake, Wisconsin, Herrin *et al.* (1998) measured average methylmercury concentrations of 186 and 100 ng/g in *Daphnia* during 1994 and 1995, respectively. Sorenson *et al.* (1990) measured an average zooplankton mercury concentration of 90 ng/g across 65 Minnesota lakes. Similarly, Tremblay *et al.* (1995) measured an average mercury concentration in zooplankton of 107.6 ng/g across 73 Canadian lakes. Plankton mercury levels measured in these studies were generally two times the levels observed in Lake Michigan. This is likely due to higher mercury concentrations in the water of these lakes than in Lake Michigan. For instance, the average surface water mercury concentration in the 65 Minnesota lakes measured by Sorenson *et al.* (1990) was 2.47 ng/L. This is more than 7 times the average total mercury concentration of 0.328 ng/L measured in Lake Michigan during the LMMB Study. Similarly, water concentrations in Devil's Lake, Wisconsin exceeded 2 ng/L. For the 73 Canadian lakes, Tremblay *et al.* (1995) did not measure water column concentrations.

7.3.2 Seasonal Considerations

Zooplankton mercury levels measured in the LMMB Study were lowest in the spring and peaked in late summer. Phytoplankton mercury levels increased throughout the summer and peaked in the fall, however, individual differences between cruises were not statistically significant for phytoplankton mercury data. The seasonal patterns of plankton mercury concentrations observed in the LMMB Study also have been documented by other researchers. In 12 northern Minnesota lakes, Monson and Brezonik

(1998) observed seasonal variations in plankton mercury concentrations with the lowest values occurring in spring and increasing throughout the summer. Similarly, Kirkwood *et al.* (1999) observed increases in phytoplankton mercury concentrations in the hypolimnion throughout the summer season in two Canadian lakes. In Devil's Lake, Wisconsin, Herrin *et al.* (1998) noted that mercury concentrations in the water of the hypolimnion increased during stratification, and that mercury concentrations in *Daphnia* peaked near the time of lake turnover in the fall (Herrin *et al*., 1998). Concentrations of methylmercury in phytoplankton and zooplankton increased two to four-fold between peak stratification and complete mixing. Herrin *et al.* (1998) concluded that mercury (particularly methylmercury) stored in the anoxic hypolimnion during summer stratification is an important source of mercury to the food chain during turnover. While plankton mercury levels measured in the LMMB Study increased in the late summer and fall as described by Herrin *et al*. (1998) in Devil's Lake, water column concentrations in Lake Michigan did not follow the same trend. No seasonal differences in epilimnetic or hypolimnetic mercury levels were observed in the LMMB Study (see Chapter 5). The Lake Michigan main lake hypolimnion is always oxic.

7.3.3 Bioaccumulation and Biomagnification

Mercury bioaccumulation factors calculated in the LMMB Study were 1.07×10^5 for phytoplankton and 1.66×10^5 for zooplankton. These bioaccumulation factors are slightly higher than reported by other researchers for other lakes in the region. Bioconcentration factors in phytoplankton and zooplankton from a north-central Wisconsin lake were approximately 3×10^4 and 5×10^4, respectively (Watras and Bloom, 1992). Similarly, bioaccumulation factors for plankton in 12 Minnesota lakes were approximately 3×10^4 (Monson and Brezonik, 1998).

In addition to bioaccumulation of mercury in the lower pelagic food web, LMMB Study results indicate the biomagnification of mercury within the lower pelagic food web. Zooplankton mercury levels were significantly higher than phytoplankton mercury levels. The biomagnification factor calculated between phytoplankton and zooplankton in the LMMB Study was 1.55. Other studies have also documented the biomagnification of mercury within the lower pelagic food web. Watras and Bloom (1992) measured higher mercury and methylmercury levels in zooplankton than phytoplankton in both reference and acidified lakes.

Tremblay *et al.* (1998) concluded biomagnification in the planktonic food web of Canadian reservoirs based on observed increases in methylmercury with increasing plankton size. Tremblay *et al.* (1998) measured biomagnification factors of 2.5 to 3 between adjacent trophic levels within the planktonic food web. These biomagnification factors are likely higher than those calculated for Lake Michigan because they are calculated based on methylmercury levels rather than total mercury levels.

While methylmercury concentrations were not measured in plankton and water during the LMMB Study, Watras and Bloom (1992) concluded that it is the methylmercury species that is most efficiently bioaccumulated and transferred up aquatic food chains. Methylmercury bioaccumulation factors were considerably higher (3×10^5 and 1×10^6 for phytoplankton and zooplankton, respectively) than bioaccumulation factors calculated based on total mercury concentrations. To further emphasize the importance of methylmercury in bioaccumulation and biomagnification, Back and Watras (1995) observed biomagnification of methylmercury from seston (which included phytoplankton and other organic suspended matter) to herbivorous zooplankton, but reported that total mercury levels did not increase between these trophic levels. Watras and Bloom (1992) also found that methylmercury becomes a progressively greater fraction of total mercury as trophic levels increase. For instance, 5% of total mercury in water was methylmercury; 13% of phytoplankton total mercury was methylmercury; 29% of zooplankton mercury was methylmercury; and >90% of fish mercury was methylmercury.

7.3.4 Other Interpretations and Perspectives

Researchers have identified various physical and chemical properties within studied lakes that have correlated with plankton mercury levels in the lakes. In general, mercury accumulation in plankton has been observed to increase with increasing water concentrations, and decreasing pH, however, researchers have not all agreed on the importance of these factors or additional factors in affecting bioaccumulation. Sorensen *et al.* (1990) found that concentrations of mercury in zooplankton from 80 northern Minnesota lakes correlated with mercury in water, mercury in fish, zooplankton density (negative correlation), pH (negative correlation), and total organic carbon. Westcott and Kalff (1996) found that water color and pH together were the best predictors of methylmercury levels in plankton from 24 Ontario lakes. Methylmercury concentrations also were positively correlated with drainage ratio and percent wetlands in the catchment (Westcott and Kalff, 1996). In contrast, Tremblay *et al.* (1995) found that zooplankton mercury concentrations in 73 Canadian lakes were poorly correlated with catchment area, primary production, total organic carbon, and sediment mercury levels. Monson and Brezonik (1998) found no correlations of plankton mercury levels with acid-neutralizing capacity, pH, dissolved organic carbon, sulfate, chlorophyll, or phosphorus in 12 northern Minnesota lakes. Back and Watras (1995) also found no relationship between total mercury in zooplankton and pH in 12 northern Wisconsin lakes.

In a direct comparison between the acidified and reference basins of Little Rock Lake, Watras and Bloom (1992) found that pH greatly influenced mercury accumulation, particularly in the methylmercury form. Mean concentrations of total mercury in phytoplankton and zooplankton were 20-30% higher in the acidified lake (pH 4.7) than in the reference lake (pH 6.1), and mean concentrations of methylmercury were 2-4 times higher in the acidified lake. The acidified conditions also appeared to greatly affect the fraction of mercury that is in the form of methylmercury. In the acidified lake, methylmercury comprised >90% of the total mercury in Cladocera, whereas <30% of total mercury in Cladocera from the non-acidified lake was methylmercury. Watras and Bloom (1992) concluded that it is the methylmercury form of mercury that is preferentially bioaccumulated and transferred up aquatic food chains, so greater proportions of methylmercury at lower trophic levels in the food chain will likely lead to greater biomagnification of mercury at higher levels of the food chain.

Later work by Watras *et al.* (1998) demonstrates that the bioaccumulation of mercury depends not only on the form of mercury under consideration (e.g., methylmercury versus inorganic mercury), but also on the particular chemical species within each form (e.g., "neutral" species such as CH_3HgCl^0 and CH_3HgOH^0 behave differently than ionized forms such as CH_3Hg^+). Some of the differences in bioaccumulation are a function of interactions and correlations with other water quality characteristics such as pH and dissolved organic carbon (DOC). The LMMB Study did not measure methylmercury in the water or all of the trophic levels of biota, nor were particular mercury species measured within any of the media. Therefore, it is unlikely that the results from this study can be used to delineate specific bioaccumulation mechanisms or pathways. Rather, the bioaccumulation factors reported in this chapter are relatively simple approximations of the transfer of mercury from the water column to the various trophic levels that are indicative of general trends in mercury concentrations.

Finally, the zooplankton data from Watras and Bloom (1992) represent results for organisms that were fractionated by size and sorted by species prior to analyses. Watras and Bloom (1992) contrast their results with bioaccumulation factors calculated from mixed assemblages of zooplankton, in which *"obscure small but important difference in bioaccumulation."* The plankton results from the LMMB Study are based on aggregate samples without regard for species. Thus, although the LMMB results demonstrate that there is bioaccumulation of mercury within the lower pelagic food web, the calculated bioaccumulation factors may not represent the accumulation that occurs between particular species within the lake ecosystem.